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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C11D 1/14, 1/16, 1/22, 1/24, 1/28, 1/29, 1/37, 1/72, 1/722, 1/825, 1/83, 1/831, 17/00, 17/08	A1	(11) International Publication Number: WO 94/21767 (43) International Publication Date: 29 September 1994 (29.09.94)
(21) International Application Number: PCT/US94/02747 (22) International Filing Date: 14 March 1994 (14.03.94) (30) Priority Data: 93870050.7 19 March 1993 (19.03.93) EP (34) Countries for which the regional or international application was filed: BE et al. 93870125.7 7 July 1993 (07.07.93) EP (34) Countries for which the regional or international application was filed: BE et al. (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): EVERS, Marc, François, Théophile [BE/BE]; Jozef Van Elewyckstraat 26 B8, B-1853 Grimbergen (BE). RENIERS, Vincent [BE/BE]; Zijdelingsestraat 19, B-3300 Tienen (BE). GEBOES, Peter, Rosalia, Joannes [BE/BE]; Kapellestraat 230, B-2630 Aartselaar (BE). MORINI, Massimo [IT/BE]; Rue Edouard-Faes 46, B-1090 Jette (BE). SCOTT, Louise, Gail [GB/BE]; Stijn Streuvelslaan 9, B-1933 Sterrebeek (BE).		(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US). (81) Designated States: AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LV, MD, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SI, SK, TJ, TT, UA, US, UZ, VN, OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: CONCENTRATED CLEANING COMPOSITIONS (57) Abstract <p>Stable and clear concentrated cleaning compositions are disclosed which comprise at least one long chain surfactant, and which are stabilized by the additional presence of short chain surfactants. The short chain surfactants further boost grease cleaning performance.</p>		

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CONCENTRATED CLEANING COMPOSITIONS

Technical Field

The present invention relates to concentrated cleaning compositions. Although the present invention relates primarily to cleaning compositions for hard surfaces, it may also be of interest for other cleaning compositions including dishwashing and laundry detergent compositions.

Background of the Invention

Concentrated cleaning compositions are well known in the art. Concentrated compositions are mainly characterized by the fact that they comprise a higher concentration of active ingredients compared to a conventional cleaning

composition, and a problem which is typically encountered when formulating concentrated cleaning compositions is therefore the physical stability of such compositions. Indeed, because such compositions comprise a high amount of active ingredients in a limited amount of water, stability problems appear which lead, if not solved, to compositions which separate into several phases. This phenomenon affects the performance of the composition and is visually noticeable, thereby rendering such formulations unfit for commercialization.

Various solutions have been proposed to solve this problem which typically involve the use of specific stabilizing ingredients, or hydrotropes. Such ingredients have the sole function of stabilizing the composition. They thus increase the cost of formulating such compositions without providing any cleaning performance benefits, and they furthermore require to free up parts in the formulation which could otherwise be used to formulate more actives.

For instance, EP 316 726 discloses concentrated compositions in the form of microemulsions which comprise water, perfume, a surfactant and a so-called co-surfactant. The co-surfactant is said to reduce the interfacial tension at interfaces between dispersed and continuous phases of an emulsion of said surfactant, thereby creating a stable microemulsion. The so-called co-surfactants in the '726 publication are listed as specific glycol ethers, which are traditionally regarded as solvents in this field, or specific carboxylic acids. The co-surfactants in the '726 publication do not appear to participate to the overall cleaning performance of the product.

It is therefore an object of the present invention to formulate a stable concentrated cleaning composition without using ingredients which are provided for the sole purpose of providing stability to the compositions herein,

but which also participate significantly to the cleaning performance of said compositions.

It has now been found that this object can be met by formulating a concentrated aqueous composition comprising a traditional long-chain surfactant, in combination with at least one short chain surfactant, i.e. with a hydrophobic group consisting of a C₆-C₁₀ alkyl chain. Said short chain surfactants provide stability to the compositions herein and, in the same time, significantly boost the overall cleaning performance, especially grease cleaning, both in neat and dilute usage.

Summary of the Invention

The compositions herein are stable clear concentrated cleaning compositions comprising from 10 % to 80 % by weight of the total composition of water, less than 15 % perfume and at least one long chain surfactant comprising a C₁₁- C₂₄ alkyl chain as its hydrophobic portion, or mixtures thereof, said compositions further comprising at least one co-surfactant consisting of a short chain surfactant comprising a C₆-C₁₀ alkyl chain as its hydrophobic portion, or mixtures thereof, except where said short chain surfactant is an alkyl ether carboxylate, said alkyl chain as said hydrophobic portion is a C₆-C₈ alkyl chain.

Detailed Description of the Invention

The compositions of the present invention are concentrated aqueous compositions. By concentrated, it is meant herein that the compositions comprise from 10 % to 80 % by weight of the total composition of water, preferably from 15 % to 75 %, most preferably from 30 % to 75 %.

The compositions according to the present invention are clear and stable. By clear and stable, it is meant herein that the compositions of the present invention are macroscopically substantially transparent, in the absence of any opacifier, and that said compositions do not macroscopically separate into separate phases during at least 1 month, at temperatures ranging from 4°C to 50°C, upon standing.

The compositions according to the present invention further comprise a long chain surfactant, or mixtures thereof. All surfactants have in common that they comprise a hydrophobic portion and a hydrophilic portion. By long chain surfactants, it is meant herein surfactants which comprise a C₁₁ to C₂₄ alkyl chain as their hydrophobic portion. Such long chain surfactants are accordingly those conventionally used in this field and can be of any type. Accordingly, suitable long chain surfactants for use herein include C₁₁-C₂₄ alkyl sulfates (C₁₁-C₂₄SO₄), alkyl ether sulfates (C₁₁-C₂₄(OCH₂CH₂)_eSO₄), alkyl sulfonates (C₁₁-C₂₄SO₃), alkyl succinates (C₁₁-C₂₄OOCH₂CH₂COOZ), alkyl carboxylates (C₁₁-C₂₄COOM), alkyl ether carboxylates (C₁₁-C₂₄(OCH₂CH₂)_eCOOM), alkyl sarcosinates (C₁₁-C₂₄CON(CH₃)R), alkyl sulfo succinates (C₁₁-C₂₄OOCH(SO₃M)CH₂COOZ), amine oxides (C₁₁-C₂₄RR'NO), glucose amides (C₁₁-C₂₄CONR''X), alkyl pyrrolidones (C₁₁-C₂₄(C₄H₆ON), alkyl polysaccharides (C₁₁-C₂₄OG_g), alkyl alkoxyates (C₁₁-C₂₄(OCH₂CH₂)_e(OCH₂CH₂CH₂)_pOH) and betaines (C₁₁-C₂₄N⁺(CH₃)₂CH₂COO⁻). In the formulae in brackets, e and p are independently from 0 to 20 and e+p>0, Z is M or R, M is H or any counterion such as those known in the art, including Na, K, Li, NH₄, amine, X is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative thereof, R, R' and R''' are C₁-C₅ alkyl groups, possibly functionalized with hydroxyl groups, R and R' are preferably C₁-C₃, most preferably

methyl, R'' is preferably 2-hydroxyethyl or 2-hydroxypropyl, G is a saccharide, preferably glucos, and g is of from 1.5 to 8. All these surfactants are well known in the art. A more complete disclosure of glucose amides can be found for instance in WO 92-06154 and a more complete disclosure of alkyl polysaccharides can be found for instance in US 4,536,319. The compositions according to the present invention may comprise any of the above surfactants alone, or any combination thereof, depending on the end use envisioned. In the compositions herein, preferred long chain surfactants are selected from long chain alkyl sulfonates and long chain alkyl ethoxylates, and mixtures thereof.

The compositions according to the present invention further comprise at least one short chain surfactant, or mixtures thereof. The definition of short chain surfactants is as above for long chain surfactants, except that said alkyl group as said hydrophobic portion is a C_6 to C_{10} alkyl group, and where said short chain surfactant is an alkyl ether carboxylate, said alkyl chain in said hydrophobic portion is a C_6 - C_8 alkyl chain. Accordingly, suitable short chain surfactants for use herein include those listed herein above in the description of long chain surfactants, but with shorter alkyl chain.

Preferred short chain nonionic surfactants for use herein are alkyl alkoxyates according to the formula C_6 - $C_{10}(OCH_2CH_2)_e(OCH_2CH_2CH_2)_pOH$, where e and p representing respectively the degree of ethoxylation and propoxylation are independently of from 0 to 20, and that $e+p>0$. Most preferred short chain nonionic surfactants for use herein are those where e and p are such that $e+p$ is from 3 to 10, particularly those where p is 0 and e is from 3 to 8. Also, most preferred short chain nonionic surfactants for use herein are those where said short chain is a hydrocarbon chain comprising from 7 to 10 carbon atoms.

Said preferred short chain nonionic surfactants for use herein can be manufactured by the processes well known to the man skilled in the art, such as condensation of the corresponding alcohol and alkylene oxide, but such short chain surfactants are more conveniently commercially available for instance from Sidobre under the trade name Mergital[®]C4 (C8EO4), from Kolb under the trade names Imbentin[®] AG/810/050 and AG/810/080 (respectively C8-10EO5 and C8-10EO8).

Preferred short chain anionic surfactants for use herein are C₆-C₁₀ alkyl sulfates (C₆-C₁₀SO₄) and alkyl sulfonates (C₆-C₁₀SO₃). Most preferred are the C₆-C₈ alkyl sulfates and sulfonates. Such short chain anionic surfactants can be made by well known sulphonation or sulphonation processes followed by neutralization, but said anionic short chain surfactants are more conveniently commercially available, for instance from Rhone Poulenc under the trade name Rhodapon[®] OLS, or from Witco under the trade name Witconate[®].

The compositions according to the present invention may comprise from 0.1 % to 50 % by weight of the total composition, preferably from 1% to 40%, most preferably from 1.5% to 30% of said short chain surfactants. The short chain surfactants herein act not only as active cleaning ingredients, but also as stabilizers. If short chain anionic surfactants are used, it is preferred to observe a minimum weight ratio of short chain anionic surfactant to longer chain surfactant of 1:10. If short chain nonionic surfactants are used, it is preferred to observe a minimum weight ratio of short chain nonionic to longer chain surfactant of 1:5.

Depending on the end use envisioned, the compositions herein may further comprise a variety of other optional

ingredients including builders, alkanolamines, pH adjusting agents, perfumes in amounts of less than 15% by weight of the total composition, dyes, bleaches, enzymes and the like.

In some instances, it may be appropriate to include a suds suppressing system in the compositions herein. Said suds suppressing system can advantageously be a mixture of 2-alkyl alkanols as described for instance in DE 40 21 265, or mixtures thereof, with a C₈ to C₂₂ fatty acid, or mixtures thereof. Such a system is particularly advantageous as both ingredients appear to act in synergy. Thus even a very low amount of said system is enough to control suds efficiently. Accordingly, said system is present in amounts of from 0.1% to 5% by weight of the total composition, preferably 0.5% to 3%.

The compositions herein do not require the presence of a stabilizing compound. By stabilizing compound, it is meant herein a compound whose sole function is to enhance the physical stability of the composition. Such compounds are typically xylene or toluene sulphonate salts, and glycol ethers, including ethylene glycol monobutyl ether, diethylene glycol monobutyl ether, dipropylene glycol monobutyl ether, dipropylene glycol methyl ether, propylene glycol methyl ether, tripropylene glycol methyl ether, propylene glycol monobutyl ether and other various solvents such as ethanol and butanol. Accordingly, the compositions of the present invention are preferably substantially free of such stabilizing compounds.

The present invention further encompasses a method of cleaning a hard surface which comprises the steps of diluting a composition according to the preceding claims in water, then applying it to said hard surface. Depending on the exact formulation, the compositions herein may be used both neat and diluted from 10 to 500 times.

Examples

The present invention will be further illustrated by the following examples.

	I	II	III	IV
C _{12/15} alkyl ethoxylate EO ₃	3	3	-	-
C _{13/15} alkyl ethoxylate EO ₇	-	-	20	-
C _{13/15} alkyl ethoxylate EO ₃₀	5	5	-	-
C _{12/14} alkyl sulfonate	-	-	-	30
C ₈ alkyl sulfate	-	10	10	10
C ₈ alkyl ethoxylate EO ₆	-	9	-	-
Citric acid	3	3	1	-
Monoethanolamine	3	3	1	-
Triethanolamine	-	-	3	-
Water & minors	-----up to 100%-----			

All compositions were evaluated for their physical stability at 4°C, at room temperature (20°C), and at 50°C. Composition I, which is not within the invention, was a gel at 4°C, and an emulsion at room temperature and at 50°C. All other compositions, within the invention, were clear transparent liquids in the same conditions.

Other compositions were made by mixing the listed ingredients in the listed proportions.

	V	VI	VII	VIII
C _{13/15} alkyl ethoxylate EO ₃	4	3	5	1
C _{13/15} alkyl ethoxylate EO ₇	-	-	-	5
C _{7/9} alkyl sulfate	7.5	-	-	-
C ₈ alkyl sulfate	-	8	-	10
C ₈ alkyl sulfonate	-	-	10	-
C _{7/9} alkyl ethoxylate EO ₆	-	-	10	5

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C _{8/10} alkyl ethoxylate EO ₅	10	9	-	9
C _{13/15} alkyl ethoxylate EO ₃₀	6	4	3	5
Na Paraffin Sulfonate	-	5	-	-
Citric acid	3	-	-	3
2-hexyl decanol	1	0.6	1	-
Palm Kernel Fatty Acid	0.4	0.4	1	-
Sodium Carbonate	-	3	-	-
Water & minors	-----up to 100%-----			

What is claimed is:

1. A stable and clear concentrated cleaning composition comprising from 10 % to 80 % by weight of the total composition of water, less than 15 % perfume and at least one long chain surfactant comprising a C₁₁-C₂₄ alkyl chain as its hydrophobic portion, or mixtures thereof, characterized in that said composition further comprises at least one co-surfactant consisting of a short chain surfactant comprising a C₆-C₁₀ alkyl chain as its hydrophobic portion, or mixtures thereof, except where said short chain surfactant is an alkyl ether carboxylate, said alkyl chain as said hydrophobic portion is a C₆-C₈ alkyl chain.
2. A composition according to claim 1 wherein said short chain surfactant or mixtures thereof represents from 0.1 % to 50 % by weight of the total composition, preferably from 1 % to 40%, most preferably from 1.5% to 30%.
3. A composition according to the preceding claims wherein said short chain surfactant, or mixtures thereof is :
 - a nonionic surfactant according to the formula C₆-C₁₀(OCH₂CH₂)_e(OCH₂CH₂CH₂)_pOH, where e and p representing respectively the degree of ethoxylation and propoxylation are independently of from 0 to 20, and that e+p>0; or
 - an anionic surfactant according to the formula C₆-C₁₀SO₄ or C₆-C₁₀SO₃; or
 - Mixtures thereof.

4. A composition according to claim 3 wherein e and p are such that e+p is from 3 to 10, preferably p is 0 and e is from 3 to 8.
5. A composition according to claim 3 wherein said anionic surfactant is $C_6-C_{10}SO_4$ or $C_6-C_{10}SO_3$.
6. A composition according to the preceding claims which comprises from 30% to 70% by weight of the total composition of water.
7. A composition according to any of the preceding claims wherein said long chain surfactants are selected from long chain alkyl sulfonates and long chain alkyl ethoxylates, and mixtures thereof.
8. A composition according to any of the preceding claims which is substantially free of stabilizing compounds.
9. A composition according to any of the preceding claims which comprises from 0.1% to 5% by weight of the total composition, preferably 0.5% to 3% of a suds suppressing system, said suds suppressing system comprising a 2-alkyl alkanol, or mixtures thereof and a C_8-C_{22} fatty acid, or mixtures thereof.
10. A method of cleaning a hard surface which comprises the steps of diluting a composition according to the preceding claims in water, then applying it to said hard surface.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/02747

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/173, 174, 174.21, 174.22, 550, 551, 552, 553, 554, 555, 557, 558, 559, DIG. 1, DIG. 14.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US, A, 5,076,954 (LOTH ET AL.) 31 December 1991 see abstract, especially lines 2-3; col. 3, lines 4-33; col. 6, lines 19-36; col. 7, line 4 - col. 10, line 23; col. 13, lines 24-38; Example 2 in col. 17.	1-5 ----- 1-5
X ---- Y	US, A, 4,671,895 (ERILLI ET AL.) 09 June 1987 see abstract; col. 4, lines 3-22; Example A in col. 4; col. 4, lines 46-47.	1-5 ----- 1-5

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	Inter document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

28 APRIL 1994

Date of mailing of the international search report

JUN 02 1994

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/02747

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 6-10
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

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2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/02747

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (5):C11D 1/14, 1/16, 1/22, 1/24, 1/28, 1/29, 1/37, 1/72, 1/722, 1/825, 1/83, 1/831, 17/00, 17/08.

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :252/173, 174, 174.21, 174.22, 550, 551, 552, 553, 554, 555, 557, 558, 559, DIG. 1, DIG. 14.